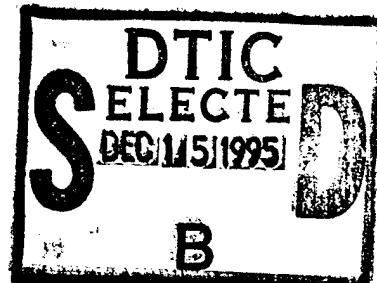


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SYNTHESIS OF  
PERFLUOROALKYLENE  
AROMATIC DIAMINES

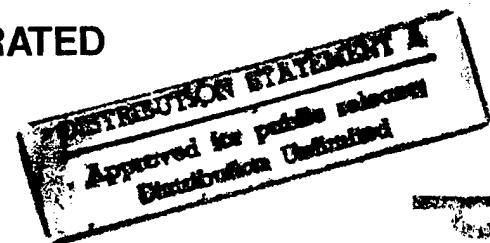


Prepared by:

K. L. Paciorek, T. I. Ito, J. H. Nakahara, and R. H. Kratzer



ULTRASYSTEMS, INCORPORATED  
Irvine, California



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## FOREWORD

This Final Report describes the work performed by Ultrasystems, Inc. during the period 14 April 1977 through 12 May 1978 under Contract NAS3-20400, "Synthesis of Perfluoroalkylene Aromatic Diamines". The investigations were carried out by K. L. Paciorek, T. I. Ito, J. H. Nakahara, and R. H. Kratzer, project manager, at the Chemicals and Materials Research Department, Irvine, California. The contract was administered by the NASA Lewis Research Center with Dr. Tito T. Serafini as the project manager.

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## 1. SUMMARY

This is the final report describing work performed by Ultrasystems, Inc. for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-20400.

The objective of this contract was to synthesize analogues of methylene dianilines in which the methylene group between the two aromatic nuclei is replaced by various perfluoroalkylene linkages and to determine the hydrolytic, thermal, and thermal oxidative characteristics of PMR Polyimides derived from these diamines.

Attempts to prepare 1,2-bis(4-aminophenyl)tetrafluoroethane were unsuccessful. 1,3-Bis(4-aminophenyl)hexafluoropropane was obtained by coupling of 1,3-diiodohexafluoropropane with p-iodoacetanilide followed by liberation of the free amine. Since 1,3-diiodohexafluoropropane is unavailable commercially it had to be synthesized from perfluoroglutarimidine.

Bromination of 2,2-bis(4-hydroxyphenyl)hexafluoropropane, Bisphenol-AF, failed to give the 4-bromo derivative. Equally unsuccessful was the direct transformation of Bisphenol-AF into the 4-amino analogue using treatment with either aniline hydrochloride or  $\text{CaCl}_2(\text{NH}_3)_x$ . Replacement of the hydroxyl group by bromine in 4-(hexafluoro-2-hydroxy-isopropyl)-aniline was accomplished; however the yield was relatively low and the product separation tedious. The desired 2,2-bis(4-aminophenyl)hexafluoropropane was obtained by coupling 4-(hexafluoro-2-hydroxy-isopropyl)-aniline and aniline in the presence of aluminum chloride.

Three types of PMR Polyimide discs were fabricated from the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid, the methyl ester of 5-norbornene-2,3-dicarboxylic acid, and one of the following three diamines:

methylene dianiline, 1,3-bis(4-aminophenyl)hexafluoropropane, and 2,2-bis(4-aminophenyl)hexafluoropropane. The polyimide based on 2,2-bis(4-aminophenyl)hexafluoropropane exhibited the best hydrolytic, thermal, and thermal oxidative characteristics as determined by moisture uptake and thermogravimetric analysis.

## 2. INTRODUCTION

Perfluoroalkyl substituents are known to enhance chemical, thermal, and oxidative stabilities of the resultant compositions as exemplified, among others, by fluorinated silicones. Based on these findings the replacement of the methylene group by perfluoroalkylene linkages in 4,4'-methylenedianiline derived PMR Polyimides (ref. 1) appeared to offer a number of potential advantages, especially with respect to hydrolytic stability. Considering the latter to be associated, at least to a degree, with the hydrophobic or hydrophilic nature of the polymer a pendant perfluoroalkyl group would seem to be the preferred arrangement. However, to assess the overall effects as compared to the fluorine-free resin both linear and branched linkages were investigated.

### 3. EXPERIMENTAL DETAILS AND PROCEDURES

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B) or under nitrogen by-pass. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Molecular weights (MW) were determined using a Mechrolab Osmometer Model 302 at concentrations of 4-6 mg/ml. Infrared (IR) spectra were recorded on double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21. Differential scanning calorimetry (DSC), differential thermal (DTA), and thermogravimetric analysis (TGA), were performed on a Du Pont 951/990 Thermal Analyzer.

All materials synthesized were dried in vacuo before physical and chemical characterization. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

#### Determination of Solubilities

Solubilities were determined by stirring the sample with alcohol for 3 hr under nitrogen by-pass to obtain a saturated solution. A measured volume (1 ml) of the supernatent solution was removed to a tared flask and the solvent distilled bulb-to-bulb to a tared collector. Values were calculated from the weights of solute and solvent.

#### Nomenclature

Since both the structural formulae and the appropriate chemical nomenclature for the monomers used during this program are complex and

cumbersome, these compounds have been coded to aid in clarity of presentation especially in polymer descriptions. The codes used are as follows:

HFD	1,3-bis(4-aminophenyl)hexafluoropropane $\text{H}_2\text{N-C}_6\text{H}_4-\text{C}(\text{F}_2)_3-\text{C}_6\text{H}_4-\text{NH}_2$
HFID	2,2-bis(4-aminophenyl)hexafluoropropane $\text{H}_2\text{N-C}_6\text{H}_4-\text{C}(\text{F}_3)_2-\text{C}_6\text{H}_4-\text{NH}_2$
MDA	4,4'-methylenedianiline $\text{H}_2\text{N-C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{NH}_2$
NE	monomethyl ester of 5-norbornene-2,3-dicarboxylic acid
BTDE	dimethyl ester of 3,3',4,4'-benzophenonetetra-carboxylic acid

Reaction of 1,2-diiodoperfluoroethane with phenylcopper

Under nitrogen by-pass to freshly prepared phenylmagnesium bromide (59.52 mmol) in ether (50 ml) was added at 2-4°C cuprous bromide (9.22 g, 32.14 mmol) over a period of 40 min. After stirring at 0-2°C for 3 hr to this mixture was added 1,2-diiodoperfluoroethane (10.96 g, 30.98 mmol) at 0-5°C over a period of 15 min. The mixture became yellow and some gas evolution was observed; analysis of the evolved gas showed it to be composed exclusively of tetrafluoroethylene. After stirring at 0-5°C for an additional 15 min a liquid aliquot was withdrawn and after hydrolysis analyzed by gas chromatography. The major product found was iodobenzene admixed with some 1,2-diiodoperfluoroethane, benzene, and traces of biphenyl. No other products were found after stirring for an additional 2 hr at 0-5°C; the product mixture following hydrolysis of the total sample

was essentially the same. It should be noted that on hydrolysis, large quantities of tetrafluoroethylene were evolved; no other fluorocarbons were detected in the gaseous products.

#### Hydrolysis of Perfluoroglutarimidine

The hydrolysis of perfluoroglutarimidine was performed following basically the procedure of W. R. Griffin (ref. 2), with the exception that the process was performed at 90°*C* inasmuch as the room temperature reaction was found to proceed very slowly. Thus, perfluoroglutarimidine (50 g) was heated with stirring in 450 ml of concentrated hydrochloric acid at 90-95°*C* for 4 hr. Subsequently the aqueous solution was continuously extracted with ether over a period of 48 hr. On removal of ether a solid-liquid mixture was obtained. Based on the facile etherate formation exhibited by perfluorinated acids (ref. 3) it was assumed that a free acid and acid etherate mixture was present. Heating of the above mixture with a small quantity of water at 90-105°*C* for 3 hr followed by removal of water at 100°*C* in *vacuo* gave 48 g (95.5% of yield) of perfluoroglutaric acid.

#### Preparation of Silver Perfluoroglutarate

To an aqueous solution of perfluoroglutaric acid (44.5 g 0.185 mol) in 30 ml water was added freshly prepared silver oxide (obtained from 70 g, 0.412 mol, of silver nitrate and 5 N sodium hydroxide); the resulting solution (containing some undissolved silver oxide) was stirred at 55°*C* for 3 hr. Subsequently the excess of silver oxide was filtered off and the clear filtrate on successive evaporation under reduced pressure in the absence of light gave (71.2 g, 85% yield) of crystalline silver salt which was dried in the dark in a desiccator over phosphorus pentoxide.

Preparation of 1,3-diiodohexafluoropropane

To a mixture of FC-43 (20 ml) and iodine (17.24 g, 67.92 mmol) in a three-neck flask equipped with nitrogen by-pass, solids addition device and distillation head (leading to a 0°C cooled receiver followed by a -78°C trap) was added silver perfluoroglutarate (5.10 g, 11.24 mmol) at 135-160°C over a period of 20 min. Heating was continued for an additional hour at which time 4.41 g of distillate was collected. This distillate was freed from elemental iodine by room temperature vacuum distillation. On standing at 0°C the liquid separated into two layers, the top layer contained mainly FC-43, whereas the bottom layer consisted essentially of 1,3-diiodohexafluoropropane. Based on GC analysis 3.82 g (84.1% yield) of the desired product was obtained.

Conducting the reaction with 25.04 g of silver perfluoroglutarate gave on purification 12.92 g (58% yield) of 1,3-diiodohexafluoropropane. Purification was accomplished by separation at -23°C of the FC-43 and 1,3-diiodohexafluoropropane layers, followed by iodine removal using copper-bronze powder.

Preparation of 1,3-bis(4-acetamidophenyl)hexafluoropropane

Copper bronze (23.52 g, 370.16 mmol) was added to a solution of 4-iodoacetanilide (24.05 g, 92.13 mmol) and 1,3-diiodohexafluoropropane (18.64 g, 46.15 mmol) in dimethylsulfoxide (95 ml). The mixture was stirred and heated under a nitrogen atmosphere for 4 hr at 120-133°C, then the cooled reaction mixture was added to water (500 ml). The suspension after stirring for ~ 5 min was filtered and washed with ether. This was followed by extraction with hot methanol (200 ml) and treatment with activated charcoal. The clear solution on cooling gave the desired product 19.31 g (78.4% yield) mp 239-240°C. Due to the compound's

insolubility in chloroform, benzene and hexafluorobenzene its molecular weight was not determined; the high melting point in conjunction with the material's low volatility prevented the obtaining of its mass spectral breakdown pattern using the probe technique.

Preparation of 1,3-bis(4-aminophenyl)hexafluoropropane

1,3-Bis(4-acetamidophenyl)hexafluoropropane (12.54 g, 29.98 mmol) obtained as described above was refluxed for 5.5 hr in a solution of concentrated hydrochloric acid (9.0 ml) and methanol (120 ml). The reaction solution was then diluted with 600 ml water and treated with sodium bicarbonate until neutral to litmus paper. The resulting emulsion was extracted with ether (4 x 100 ml) and the combined extracts washed with water (5 x 200 ml), dried over anhydrous magnesium sulfate, filtered, and the filtrate evaporated to give a yellow oil (11.2 g). The oil was then treated with hot cyclohexane and the combined extracts were concentrated, treated with activated charcoal, filtered and cooled to give 3.53 g (35.2%) of the desired product, mp 67.5-68.5°C. The DTA scan is presented in Figure 1. Anal. Calcd. for  $C_{15}H_{12}F_6N_2$ : C, 53.90; H, 3.62; F, 34.10; N, 8.38; MW, 334.26. Found: C, 54.56; H, 3.81; F, 33.59; N, 8.34; MW, 331.

The structure was confirmed by mass spectral analysis wherein the molecular peak as well as characteristic breakdown fragments were observed. The mass spectrum is given in Table I. The solubility in methanol was measured as 3.0095 g/ml; in ethanol 1.8989 g/ml.

The alcohol treatment resulted in ~50% material transformation into what appears to be  $H_2NC_6H_4CO(CF_2)_2C_6H_4NH_2$ , mp 136-137.5°C, based on its mass spectral breakdown pattern given in Table II.

Attempted Preparation of 2,2-bis(4-bromophenyl)hexafluoropropane

a) Via reaction of 2,2-bis(4-hydroxyphenyl)hexafluoropropane (Bisphenol-AF) with phosphorus pentabromide in the absence of solvent

Bisphenol-AF (5.09 g, 15.14 mmol) was mixed with phosphorus pentabromide (12.90 g, 29.74 mmol) and heated under nitrogen by-pass for 6 hr at 100-122°C. Treatment with water gave 12.68 g of material which was then further purified by dissolution in aqueous potassium hydroxide; most dissolved indicating that phenolic groups remained. Acidification of the solution gave a solid which based on its infrared spectrum consisted essentially of the starting material admixed possibly with bromosubstituted aromatics.

b) Via reaction of Bisphenol-AF with phosphorus pentabromide in bromobenzene

The solvent was utilized to provide a homogeneous reaction mixture inasmuch as under conditions employed in (a) a solid remained throughout the heating process. Thus a mixture of Bisphenol-AF (2.07 g, 6.16 mmol), phosphorus pentabromide (5.36 g, 12.45 mmol) and bromobenzene (5 ml) was heated at 70-100°C for 1.5 hr, then at 120-125°C for 5 hr. The cooled reaction mixture was treated with water and extracted with ether. Removal of ether gave 2.55 g of residue which on crystallization from ether-petroleum ether yielded 1.21 g (40% yield) of 2,2-bis(4-hydroxy-x-bromophenyl)hexafluoropropane, mp 148-153°C. The structure was elucidated from the mass spectral breakdown pattern (see Table III).

Attempted Preparation of 2,2-bis(4-aminophenyl)hexafluoropropane, via reaction of Bisphenol-AF with aniline hydrochloride

a) At 175-200°C under atmospheric pressure

Heating a 1:5 mixture of Bisphenol-AF and aniline hydrochloride

at 175-200°C over a period of 4 hr resulted in the sublimation of aniline hydrochloride and recovery of the Bisphenol-AF.

b) At 190°C in a sealed ampoule

Heating Bisphenol-AF (4.40 g) with aniline hydrochloride (6.78 g) at 190°C for 48 hr resulted in quantitative Bisphenol-AF recovery.

c) At 250 and 290°C in a sealed ampoule

Heating Bisphenol-AF (5.53 g) with aniline hydrochloride (8.53 g) at 250°C for 160 hr gave ~ 7% yield of diphenylamine identified by GC-MS; 82% of Bisphenol-AF was recovered. Conducting the reaction at 290°C for 42 hr increased only the yield of diphenylamine; no 2,2-bis(4-aminophenyl)-perfluoropropane was produced.

Treatment of Bisphenol-AF with  $\text{CaCl}_2(\text{NH}_3)_x$

W. Borsche and M. Wagner - Roemmich (ref. 4) do not specify the number of ammonia moieties present in  $\text{CaCl}_2(\text{NH}_3)_x$ . Compounds of composition  $\text{CaCl}_2(\text{NH}_3)_x$  wherein  $x = 1, 2, 4$  and 8 are known (ref. 5,6). It has been found here that to prepare any of these adducts, calcium chloride must be absolutely anhydrous. In view of the high vapor pressure at room temperature of  $\text{CaCl}_2(\text{NH}_3)_4,8$  treatment of  $\text{CaCl}_2$  with liquid ammonia gave after removal in vacuo of the excess ammonia the composition  $\text{CaCl}_2(\text{NH}_3)_{2.5}$  (mainly  $\text{CaCl}_2(\text{NH}_3)_2$  admixed with some  $\text{CaCl}_2(\text{NH}_3)_4$ ). Thus a mixture of Bisphenol-AF (0.28 g, 0.83 mmol) and  $\text{CaCl}_2(\text{NH}_3)_{2.5}$  (0.97 g, 6.32 mmol) was heated in a sealed, evacuated ampoule at 300°C for 160 hr. The solid (0.21 g) obtained after water treatment of the reaction mixture followed by solvent extraction was found to consist essentially of the starting material, Bisphenol-AF, admixed with some phenol. Based on mass spectral analysis none of the desired 2,2-bis(4-aminophenyl)-hexafluoropropane was formed.

Preparation of 4-(hexafluoro-2-hydroxy-isopropyl)aniline

Under nitrogen by-pass, in an apparatus equipped with dry ice condenser and addition funnel, into aniline (9.50 g, 102.01 mmol) at 170°<sup>o</sup>C was added hexafluoroacetone hydrate (20.16 g, 104.43 mmol) over a 2 hr period. After an additional hr at 170°<sup>o</sup>C the hot liquid was poured into a beaker and the solid mass obtained on cooling was then crystallized from ether-petroleum ether giving the desired product, 11.08 g (42% yield) mp 149-150°<sup>o</sup>C (ref. 7, 149-150°<sup>o</sup>C).

Attempted Preparation of 2,2-bis(4-aminophenyl)hexafluoropropane

a) Using aluminum chloride catalysis

A mixture of 4-(hexafluoro-2-hydroxy-isopropyl)aniline (1.90 g, 7.33 mmol) was heated under nitrogen by-pass with aluminum chloride (1.02 g, 7.65 mmol) and aniline (2.75 g, 29.53 mmol) at 170°<sup>o</sup>C for 4 hr. The black mixture obtained on cooling was taken up in ether and washed with water. From the residue obtained after solvent and aniline removal the starting material was quantitatively recovered.

b) Using p-toluenesulfonic acid catalysis

A mixture of 4-(hexafluoro-2-hydroxy-isopropyl)aniline (1.94 g, 7.49 mmol) was heated under nitrogen by-pass with p-toluenesulfonic acid (30 mg, 0.15 mmol) and aniline (1.42 g, 15.25 mmol) at 180°<sup>o</sup>C for 4 hr. After removal of aniline the starting material was quantitatively recovered.

Treatment of 4-(hexafluoro-2-hydroxy-isopropyl)aniline with phosphorus pentabromide

a) At 87-93°<sup>o</sup>C

A mixture of 4-(hexafluoro-2-hydroxy-isopropyl)aniline (3.63 g,

14.01 mmol) and phosphorus pentabromide (6.29 g, 14.61 mmol) was heated under nitrogen by-pass at 87-93°C for 2 hr; a red pasty material resulted. Trituration with cold petroleum ether resulted in isolation of 1.85 g (51%) of the starting material as an insoluble solid. The petroleum ether fractions on evaporation yielded a liquid admixed with some solid. The solid (0.37 g, 8.2% yield) was manually separated from the liquid and crystallized from ether-petroleum ether, mp 130-131°C. Its infrared spectrum was different from that of the starting material and the mass spectrum indicated that one of the hydrogens (most likely on the ring) was substituted by bromine (m/e, 337).

b) At 93-122°C

A mixture of 4-(hexafluoro-2-hydroxy-isopropyl)aniline (1.68 g, 6.48 mmol) and phosphorus pentabromide (2.79 g, 6.48 mmol) was heated under nitrogen by-pass at 93-100°C for 1 hr, then at 100 to 122°C for another 1 hr, and finally at 122°C for 2 hr. A dark colored liquid resulted. This material was treated with water at 0°C and neutralized with concentrated potassium hydroxide solution. Subsequently, the mixture was extracted with ether. On removal of ether the remaining tacky material was treated with petroleum ether giving a powdery solid (0.93 g, 44% yield). Crystallization from ether-petroleum ether gave a material with mp 141-143°C; based on mass spectral analysis it contained 70% of the desired product  $\text{H}_2\text{N-C}_6\text{H}_4-\text{C}(\text{CF}_3)_2\text{Br}$ , admixed with  $\text{H}_2\text{N-C}_6\text{H}_4-\text{C}(\text{CF}_3)_2\text{OH}$  and  $\text{H}_2\text{N-C}_6\text{H}_3\text{Br-C}(\text{CF}_3)_2\text{OH}$ . The material wherein the hydroxyl group was substituted by bromine was identified by its parent peak at m/e 322 and the characteristic mass spectral breakdown pattern.

Treatment of 4-(hexafluoro-2-hydroxy-isopropyl)aniline with aniline and aluminum chloride

a) Using excess of aluminum chloride, in a sealed ampoule

A mixture of 4-(hexafluoro-2-hydroxy-isopropyl)aniline (2.06 g, 7.95 mmol), aluminum chloride (8.26 g, 61.95 mmol) and aniline (1.46 g, 15.68 mmol) was sealed in vacuo and heated in a furnace at 200°C for 66 hr. Subsequently the ampoule was cooled, the evolved hydrogen chloride vented and the black reaction mixture poured onto ice. The aqueous solution (400 ml) was neutralized with sodium hydroxide and extracted with ether. The reddish material (0.90 g) obtained on evaporation of ether consisted of a mixture of aniline and benzidine as determined by GC-MS analysis. No 2,2-bis(4-aminophenyl)hexafluoropropane was detected. The original black, acid insoluble residue was extracted with ether and benzene and this process was repeated after treatment with base. Only a trace, ~ 100 mg, of material was thus extracted and it did not contain the desired product.

b) Using a 4-(hexafluoro-2-hydroxy-isopropyl)aniline to aluminum chloride ratio of 1:1

A mixture of 4-(hexafluoro-2-hydroxy-isopropyl)aniline (11.50 g, 44.38 mmol), aluminum chloride (6.21 g, 46.57 mmol), and aniline (16.58 g, 178.03 mmol) was heated under nitrogen by-pass for 116 hr at 186-198°C. After cooling, water (400 ml) was added and the mixture was continuously extracted with ether for 40 hr. The ethereal solution was then washed with 10% hydrochloric acid (800 ml); neutralization of the acidic aqueous solution followed by ether extraction gave 4.94 g of a semisolid mass which consisted of 23% of the desired product and 30.5% of the starting material, 4-(hexafluoro-2-hydroxy-isopropyl)aniline,

admixed with diphenylamine and aniline. To isolate 2,2-bis(4-amino-phenyl)hexafluoropropane the semisolid mass was washed with a small quantity of benzene and the residue was sublimed at 70-85°C to remove any starting material. The sublimation residue consisted of pure 2,2-bis-(4-aminophenyl)hexafluoropropane (which itself sublimed readily at 95°C); mp 190-193°C (after crystallization from benzene); the DSC scan is given in Figure 2. Anal. Calcd. for C<sub>15</sub>H<sub>12</sub>F<sub>6</sub>N<sub>2</sub>: C, 53.90; H, 3.62; F, 34.10; N, 8.38. Found: C, 54.27; H, 3.68; F, 35.59; N, 8.13.

The structure was confirmed by mass spectral analysis wherein the molecular peak together with characteristic breakdown fragments were observed. The mass spectrum is given in Table IV.

Solubility was determined to be 0.1726 g/ml in methanol; 0.1168 g/ml in ethanol.

#### Preparation of BTDE/MDA/NE, 1500 FMW Resin

To a methanolic solution of BTDE (prepared from BTDA (17.05 mmol) and methanol) were added at ambient temperature MDA (5.00 g, 25.23 mmol), NE (3.21 g, 16.34 mmol) and methanol (8.21 g). The solvent was then removed in an air circulating oven at 120°F over a period of 69 hr affording 13.86 g of the uncured product; this was imidized at 390-400°F over a period of 3 hr.

#### Preparation of BTDE/HFD/NE, 1636 FMW Resin

To a methanolic solution of BTDE (prepared from BTDA (1.21 mmol) and methanol) were added at ambient temperature HFD (0.601 g, 1.79 mmol), NE (0.229 g, 1.16 mmol) and methanol (0.827 g). The mixture was stirred until a solution resulted. The solvent was removed in an air circulating oven at 158-167°F. The solid was subsequently dried at 167°F

over a period of 20 hr and this was followed by imidization for 3 hr at 390-400° F.

#### Preparation of BTDE/HFID/NE, 1636 FMW Resin

To a solution of BTDE (prepared from BTDA (4.05 mmol) and methanol) in methanol were added at ambient temperature HFID (2.001 g, 5.99 mmol), NE (0.761 g, 3.88 mmol) and methanol (2.761 g). The mixture was then stirred overnight to permit complete dissolution of HFID. The solvent was then removed in an air circulating oven at 160° F. The solid was subsequently dried at 160-170° F over a period of 21 hr and this was followed by imidization for 3 hr at 390-400° F.

#### Preparation of Discs

A number of procedures were explored for the preparation of the fully cured discs. It was found that best results were obtained by using pre-imidized material and conducting the cure in the 0.5" die by initially compressing the sample at room temperature at 2500 psi for ~ 24 hr, raising the temperature to ~ 400° F with the same pressure applied, then reducing to contact pressure while gradually heating from 400° F to 600° F over a period of 3 hr, followed by treatment at 600° F for 1.5 hr. Cooling was also gradual (2 hr, 600 to 150° F). The discs were post-cured by placing the disc (mold set in a C-clamp) into an oven at 570-581° F (4 hr), followed by an increase of temperature (15-30 min) to 650° F and finally 1 hr residence at 650° F. The mold was removed and cooled. The discs were well formed.

#### Hydrolytic Stability Testing

Weighed discs were placed in a desiccator containing an aqueous solution of sodium sulfate (15% by weight) calculated to give a humidity of ~ 95% at 25° C (ref. 8). The exposure time was 30 days. The weight

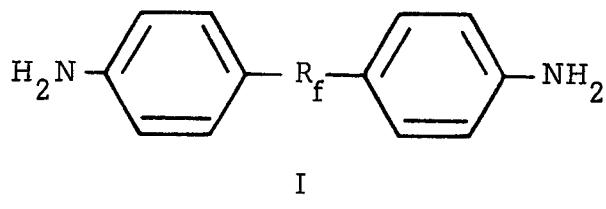
gain-time relationship is given in tabular form in Table V, and as a graphical presentation in Figure 3. The results of thermogravimetric studies performed on the polyimides are summarized in Table VI.

#### 4. TECHNICAL DISCUSSION

The objective of this contract was to prepare analogues of methylene dianilines in which the methylene group between the two aromatic nuclei is replaced by various perfluoroalkylene linkages. These diamines were then to be used to prepare polyimides using the PMR technique (ref. 1) and the resulting products evaluated in regard to their thermal, oxidative, and hydrolytic stabilities.

##### 4.1 MONOMER SYNTHESIS

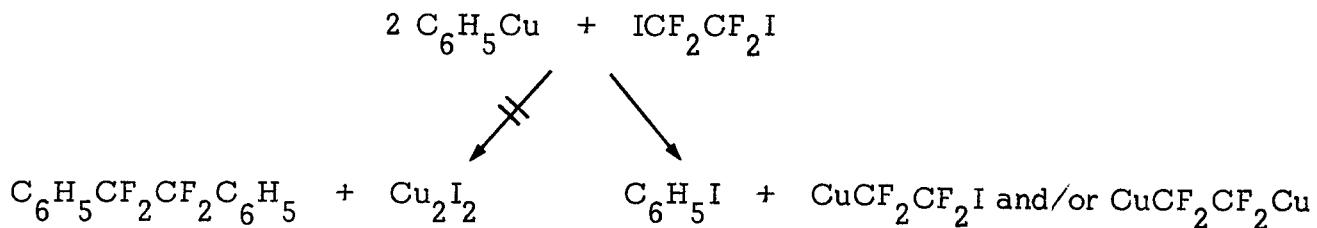
A number of potential synthetic routes exist for the preparation of perfluoroalkylene linked aromatic materials such as e.g., perfluoroalkylene linked diamines,



Generally the simplest procedure to obtain perfluoroethylene linked aromatics is the interaction of the perfluoroalkyl diiodide with bromo- or iodo-substituted aromatics. Tetrafluoroethylene is commercially available and the simple interaction with iodine affords the diiodoethane in essentially quantitative yield. Consequently, materials derived from reaction of 1,2-diiodotetrafluoroethane appeared economically attractive.

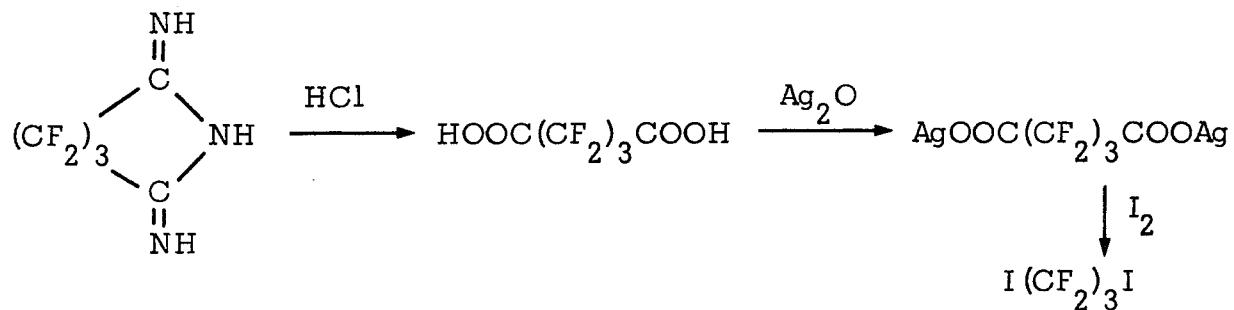
Past work (ref. 9) has shown that direct reaction of an aromatic halide with 1,2-diiodotetrafluoroethane using copper-bronze in DMSO resulted in tetrafluoroethylene liberation at temperatures above 40°C necessary to initiate the reaction. It was hoped that treatment of

phenylcopper in ethereal suspension at low temperature with 1,2-diiodotetrafluoroethane would result in the desired coupling.

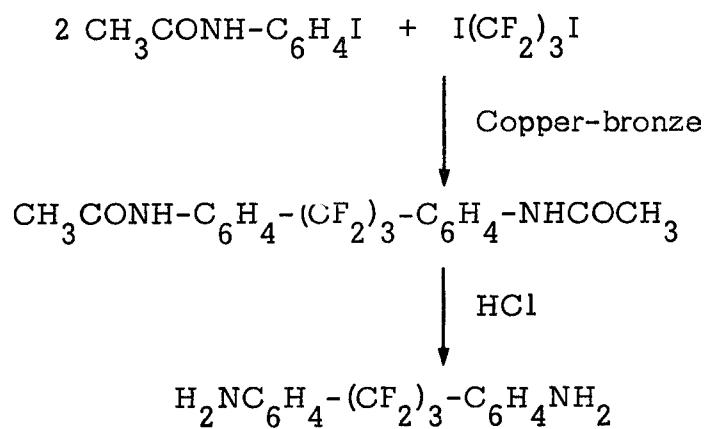


Unfortunately instead of coupling an exchange giving iodobenzene and 1-copper-2-iodotetrafluoroethane and/or possibly 1,2-dicoppertetrafluoroethane took place. One would expect  $\text{CuCF}_2\text{CF}_2\text{I}$  to liberate tetrafluoroethylene readily, whereas  $\text{CuCF}_2\text{CF}_2\text{Cu}$  would be unlikely to do so. It should be noted that during addition of 1,2-diiodotetrafluoroethane to the phenylcopper suspension some tetrafluoroethylene was liberated (indicating formation and decomposition of  $\text{CuCF}_2\text{CF}_2\text{I}$ ); however, the bulk of tetrafluoroethylene was formed only on hydrolysis of the reaction mixture. Since no tetrafluoroethane was observed in the evolved gases, it seems safe to assume that no dicopper compounds were formed.

For 1,3-diiodohexafluoropropane, where no tendency exists to liberate iodine with formation of an olefin, it was shown (ref. 9, 10) that coupling with a variety of aromatic iodides in the presence of copper-bronze can be successfully accomplished. Unfortunately, 1,3-diiodohexafluoropropane is unavailable commercially and thus had to be prepared from perfluoroglutarimidine, which was kindly donated by Mr. W. R. Griffin of the Air Force Materials Laboratory. Below is presented the reaction path to the desired diiodo-compound:

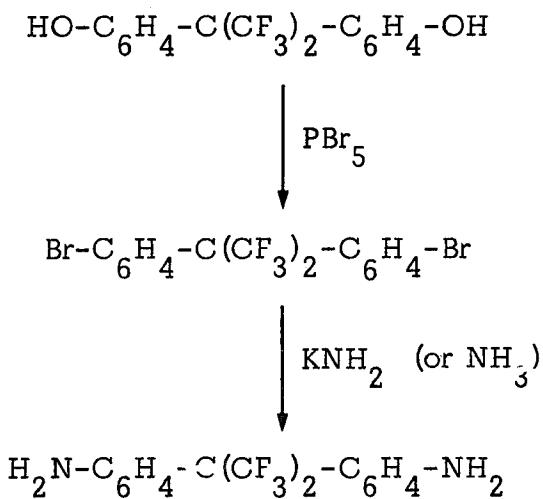


In the case of silver perfluoroglutarate the conventional Hunsdiecker reaction, wherein the salt and iodine are mixed together and heated, was found to give very low yields of the diiodide due to predominant lactone formation (ref. 11). W. R. Griffin (ref. 2) discovered that the yield can be improved using FC-43 as the solvent. Accordingly, to the iodine in hot FC-43 was added the solid silver salt; yields ranging from 84-58% were realized using this procedure. The direct copper-bronze coupling of p-iodoaniline with 1,3-diiodohexafluoropropane did not yield the desired 1,3-bis(4-aminophenyl)hexafluoropropane. However, using p-iodoacetanilide, 1,3-bis(p-acetamidophenyl)hexafluoropropane was obtained in 78% yield, and it gave the free amine on hydrolysis in 35% yield i.e.:



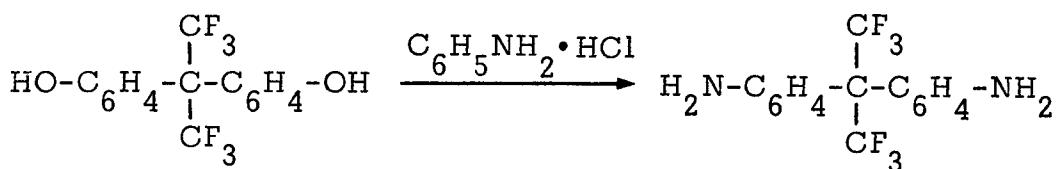
The amine appears to be thermally and hydrolytically unstable as indicated by the exotherm at  $\sim 110^{\circ}\text{C}$  in its DTA scan (see Figure 1) and by the low degree of material recovery after determining the solubility in alcohols. The instability would thus explain the low yields realized on preparation of the free dianiline from the acetanilide and the inability to conduct the coupling directly. Based on mass spectral analysis (see Table II) the major degradation product seems to be  $\text{H}_2\text{NC}_6\text{H}_4\text{COCF}_2\text{CF}_2\text{C}_6\text{H}_4\text{NH}_2$ .

To produce a material wherein the  $R_f$  moiety of the basic structure I is  $\text{C}(\text{CF}_3)_2$ , one of the most promising avenues would appear to be the transformation of Bisphenol-AF,  $\text{HO-C}_6\text{H}_4-\text{C}(\text{CF}_3)_2-\text{C}_6\text{H}_4-\text{OH}$ , inasmuch as this compound is commercially available. The route via a dibromo compound, although consisting of a two step sequence, appeared especially attractive i.e.



Unfortunately, phosphorus pentabromide failed to exchange the hydroxyl group with bromine; instead ring bromination occurred giving thus a 40% yield of 2,2-bis(4-hydroxy- $\alpha$ -bromophenyl)hexafluoropropane.

Krimm et al (ref. 12) prepared 2,2-bis(4-aminophenyl)propane from the corresponding hydroxy compound via treatment with aniline hydrochloride at  $\sim 180^{\circ}\text{C}$ . Thus extending this process to Bisphenol-AF was an obvious choice, i.e.:



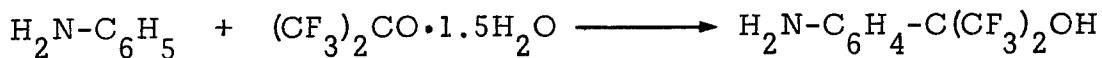
However, heating Bisphenol-AF with aniline hydrochloride below  $200^{\circ}\text{C}$  gave quantitative starting material recovery. Between  $250\text{-}290^{\circ}\text{C}$  the only product formed was diphenylamine.

The transformation of a phenolic moiety into an amino group has been reported (ref. 4) using  $\text{CaCl}_2(\text{NH}_3)_x$  at  $250\text{-}270^{\circ}\text{C}$ . In the case of Bisphenol-AF this reaction leads to rupture of the phenyl-perfluoroisopropyl linkage with concomitant formation of phenol.

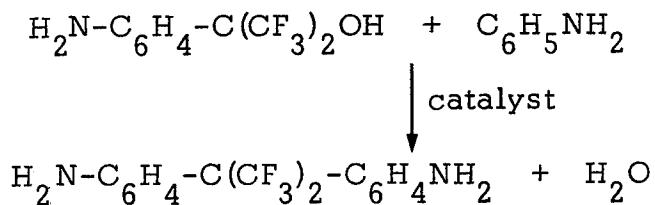
Based on the above unsuccessful transformation attempts it is obvious that the perfluoroalkyl bridging group has a much more pronounced effect upon the reactivity and behavior of the hydroxyl groups than would appear just from the consideration of the electrophilic nature of this moiety. Furthermore, as can be seen from the formation of phenol, the perfluoroisopropyl group itself can be involved in reactions preventing the desired process or processes from occurring.

Bisphenol-AF itself is obtained from the reaction of hexafluoroacetone and phenol in the presence of hydrogen fluoride at  $100^{\circ}\text{C}$  (ref. 13,14). It has been reported that aniline at  $170\text{-}200^{\circ}\text{C}$  gives 4-(hexafluoro-2-hydroxyisopropyl)aniline (ref. 6). This material is a potential precursor of 2,2-bis-(4-aminophenyl)hexafluoropropane. Accordingly, 4-(hexafluoro-2-hydroxyisopropyl)aniline was prepared from hexafluoroacetone hydrate and aniline

in 42% yield following essentially the procedure of Gilbert, et al (ref. 7) although these investigators utilized hexafluoroacetone itself which is no longer commercially available:

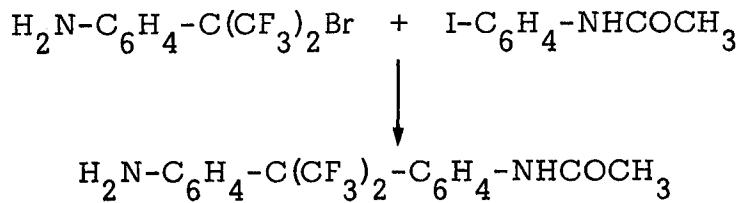


Attempts were made to couple this material with additional quantities of aniline in the presence of aluminum chloride and p-toluenesulfonic acid, i.e.,

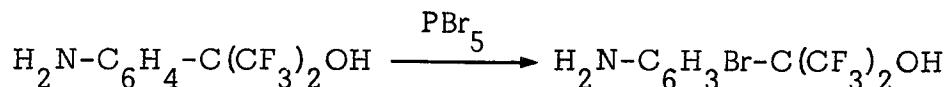


However, utilizing reaction times comparable to those employed in the synthesis of 4-(hexafluoro-2-hydroxy-isopropyl)aniline the starting materials were recovered essentially quantitatively.

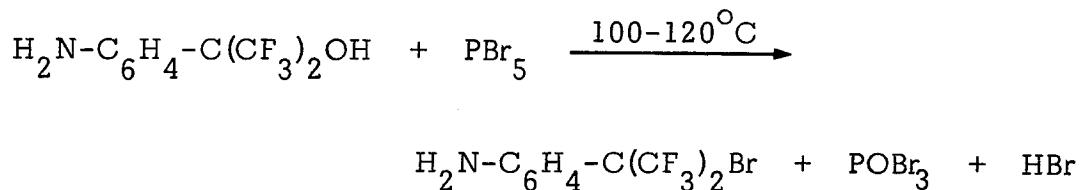
In view of the pronounced ability of perfluoroalkyl halides to couple with iodobenzene derivatives in the presence of copper bronze and the ready formation of the hexafluoroisopropanol derivative it seemed worthwhile to attempt the replacement of the hydroxy group by a bromine atom. The resulting bromide would then be expected to couple with p-iodoacetanilide using the copper-bronze DMSO procedure, i.e.:



Treatment of 4-(hexafluoro-2-hydroxy-isopropyl)aniline with phosphorus pentabromide below 95°C resulted in 50% starting material recovery and in the isolation of ~ 5% of ring brominated products as determined by mass spectral analysis, i.e.,



Conducting the phosphorus pentabromide reaction at 100-120°C gave a 45% yield of a product mixture which contained ~ 70% of the desired product admixed with the starting material and the ring brominated compounds:



The low yield of the desired product, together with the difficulties associated with its isolation and the unknown prospects of the next required coupling step made this approach less attractive than the reinvestigation of the direct reaction.

Interaction of 4-(hexafluoro-2-hydroxy-isopropyl)aniline with aniline and aluminum chloride at 190°C for 65 hr using an aluminum chloride to 4-(hexafluoro-2-hydroxy-isopropyl)aniline ratio of 8 to 1 gave as the only diamino-compound benzidine. However, employing a 1:1 reagent ratio and a four fold excess of aniline afforded the desired 2,2-bis(4-aminophenyl)-hexafluoropropane in 10% yield as determined by GC-MS analysis. The product was identified by comparison of its GC-retention time, melting

point, mass and infrared spectra with that of an authentic sample. The mass spectrum of 2,2-bis(4-aminophenyl)hexafluoropropane is given in Table IV. It should be noted that the m/e peaks 334, 335 (molecular weight) and 265 (loss of  $\text{CF}_3$  group) are characteristic for this compound. It is believed that this process could be optimized to afford yields in excess of the reported 10%, but this was not within the scope of the program.

#### 4.2 POLYMER INVESTIGATIONS

Three PMR Polyimides, namely BTDE/MDA/NE (1500 FMW), BTDE/HFD/NE (1636 FMW), and BTDE/HFID/NE (1636 FMW) were prepared using the PMR technique. The imidization, fabrication and curing conditions employed are fully described in the experimental section.

The moisture absorption characteristics of the cured discs were determined by exposure to a 95% humidity atmosphere for 30 days at room temperature. As can be seen from Table V and the graphical presentation given in Figure 3 the absorption process reached a steady state between 2 and 9 days. In agreement with predictions BTDE/HFID/NE exhibited the least moisture absorption. The behavior of BTDE/HFD/NE resin is not really surprising if one considers the instability of the parent diamine.

The thermal and thermal oxidative characteristics of these discs were determined by TGA, both prior and after exposure to the 95% humidity environment. The results of these tests are summarized in Table VI. The temperature region considered in this tabulation, namely weight loss up to  $400^{\circ}\text{C}$ , has been selected since this appears to be the stability limit

of this resin system based on TGA. Examining the data it can be deduced that in nitrogen BTDE/HFID/NE polyimide loses all the absorbed moisture without any retention or increased degradation. In air the presence of moisture seems to promote oxidation since the weight loss at 400<sup>o</sup>C (2.75%) is somewhat less than the sum of moisture absorbed plus the weight loss of the untreated sample (1.76 + 1.25). This effect is evident to a significantly larger extent in the BTDE/MDA/NE resin and is most pronounced in the BTDE/HFD/NE materials.

## 5. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are conclusions and recommendations reached during the current investigations of perfluoroalkylene aromatic diamines as potential candidates in polyimide optimization.

- 1) Two diamines were synthesized, 1,3-bis(4-aminophenyl)hexafluoropropane and 2,2-bis(4-aminophenyl)hexafluoropropane.
- 2) The hydrolytic, thermal and thermal oxidative stability of the 2,2-bis(4-aminophenyl)hexafluoropropane derived polyimide was found to be superior to that of methylenedianiline and 1,3-bis(4-aminophenyl)hexafluoropropane derived resins.
- 3) The presence of difluoromethylene groups next to the aromatic ring appears to impart the observed hydrolytic instability of 1,3-bis(4-aminophenyl)hexafluoropropane, whereas the perfluoroisopropyl linkage provides the desired hydrophobic properties without any decrease in the thermal and thermal oxidative stability of the resultant polyimide.
- 4) The synthesis of 2,2-bis(4-aminophenyl)hexafluoropropane via interaction of 4-(hexafluoro-2-hydroxy-isopropyl)aniline with aniline and aluminum chloride gave the desired product in only 10% yield. This process should and most likely can be optimized to achieve more reasonable yields.

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TABLE I  
ION FRAGMENTS AND INTENSITIES RELATIVE  
TO BASE PEAK OF  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-(\text{CF}_2)_3-\text{C}_6\text{H}_4-\text{NH}_2$ <sup>a</sup>

m/e		m/e	
20	3.0	115	4.0
32	8.9	122	2.0
39	2.4	125	2.0
65	4.5	142	<u>100.</u>
92	2.0	143	8.0
93	2.0	173	5.7
95	4.5	334	32.5
114	2.6	335	5.4

a) Peaks having intensities less than 2% of the base peak are not reported.

TABLE II  
ION FRAGMENTS AND INTENSITIES RELATIVE  
TO BASE PEAK OF  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{CF}_2\text{CF}_2\text{C}(\text{O})\text{C}_6\text{H}_4-\text{NH}_2$ <sup>a</sup>

m/e		m/e	
20	3.3	115	4.0
39	5.7	120	<u>100.</u>
65	28.2	121	21.4
66	5.4	122	3.3
78	4.6	142	51.3
91	6.8	143	6.8
92	31.3	173	3.6
93	3.7	312	32.4
95	3.3	313	10.5

a) Peaks having intensities less than 3% of the base peak are not reported.

TABLE III  
ION FRAGMENTS AND INTENSITIES RELATIVE TO  
BASE PEAK OF  $\text{H}_2\text{N-C}_6\text{H}_3\text{Br-C}(\text{CF}_3)_2\text{-C}_6\text{H}_3\text{Br-NH}_2$ <sup>a</sup>

m/e		m/e		m/e	
69	65.4	113	13.8	237	12.1
74	11.4	125	11.4	265	72.0
75	21.1	132	33.2	266	14.2
79	73.7	137	10.4	275	23.2
80	92.4	138	20.1	277	24.6
81	66.8	139	26.6	344	20.4
82	<u>100.</u>	167	12.1	346	18.3
83	29.8	168	26.6	413	10.4
84	19.7	169	10.7	423	42.6
85	26.3	188	11.8	425	72.7
93	20.1	197	29.4	426	11.1
97	13.1	207	11.1	427	38.4
98	17.6	215	11.1	492	17.0
99	16.6	217	13.5	494	35.3
107	19.0	236	32.5	496	22.5

a) Peaks having intensities less than 10% of the base peak are not reported.

TABLE IV  
ION FRAGMENTS AND INTENSITIES RELATIVE TO  
BASE PEAK OF  $\text{H}_2\text{N-C}_6\text{H}_4\text{-C}(\text{CF}_3)_2\text{-C}_6\text{H}_4\text{-NH}_2$ <sup>a</sup>

m/e		m/e		m/e	
52	5.2	142	8.2	198	14.8
63	5.1	151	6.4	225	10.6
65	10.5	152	5.6	245	6.0
77	5.0	167	17.8	248	7.3
78	7.5	168	17.6	249	7.4
83	12.3	178	6.9	264	24.1
84	5.3	179	9.3	265	<u>100.</u>
89	6.0	180	24.1	266	40.7
92	6.2	181	5.3	315	7.6
93	5.1	194	5.3	333	6.3
97	23.2	195	55.8	334	85.3
98	53.6	196	30.2	335	26.7
133	48.2	197	5.4		

a) Peaks having intensities less than 5% of the base peak are not reported.

TABLE V

WEIGHT GAIN OF FULLY CURED RESINS ON EXPOSURE  
TO 95% HUMIDITY

Sample	Weight Percent Gain				
	Day 1	Day 9	Day 16	Day 23	Day 30
BTDE/MDA/NE	1.17	2.18	2.44	2.50	2.52
BTDE/HFD/NE	2.95	3.87	3.94	4.08	4.15
BTDE/HFID/NE	1.35	1.69	1.73	1.73	1.76

TABLE VI

GRAVIMETRIC INVESTIGATION OF POLYIMIDE RESINS

Compound	95% Humidity Exposure <sup>a</sup>		TGA <sup>b</sup> Weight Loss between 100-400°C	
	Sample Weight mg	Weight Gain %	Post Cured Samples	
			N <sub>2</sub>	Air
BTDE/MDA/NE	384.7	2.52	2.50 (Fig. 4)	2.50 (Fig. 5)
BTDE/HFD/NE	291.8	4.15	3.13 (Fig. 8)	2.75 (Fig. 9)
BTDE/HFID/NE	295.6	1.76	1.25 (Fig. 12)	1.25 (Fig. 13)

a) All the materials exposed to the 95% humidity for 30 days were post cured.

b) The numbers in parenthesis show the weight loss value correspond to number of the figures given in Appendix.

PART NO. 990088

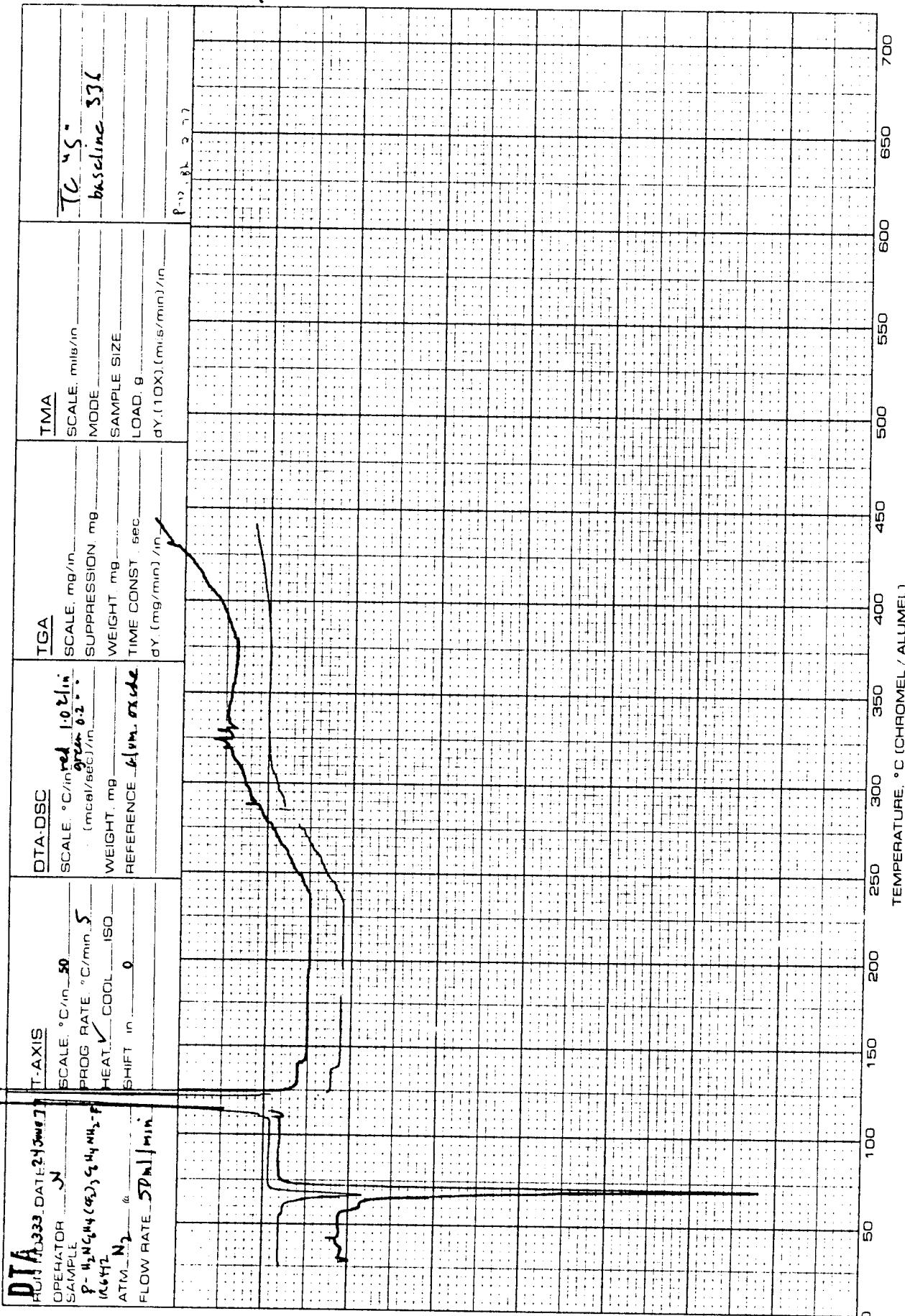
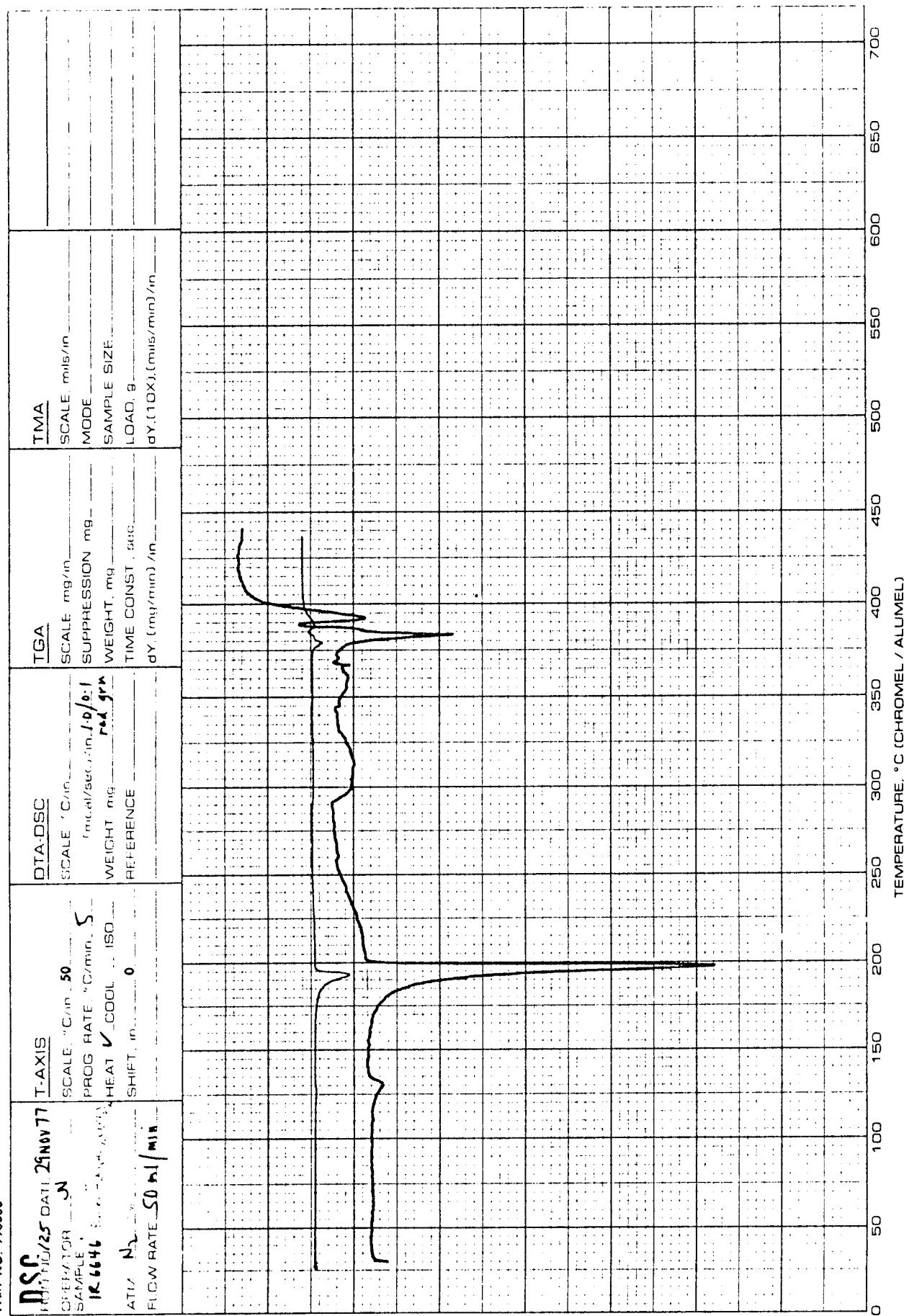


Figure 1: DTA Scan of 1,3-Bis(4-aminophenyl)hexafluoropropane

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Figure 2: DSC Scan of 2,2-Bis(4-aminophenyl)hexafluoropropane

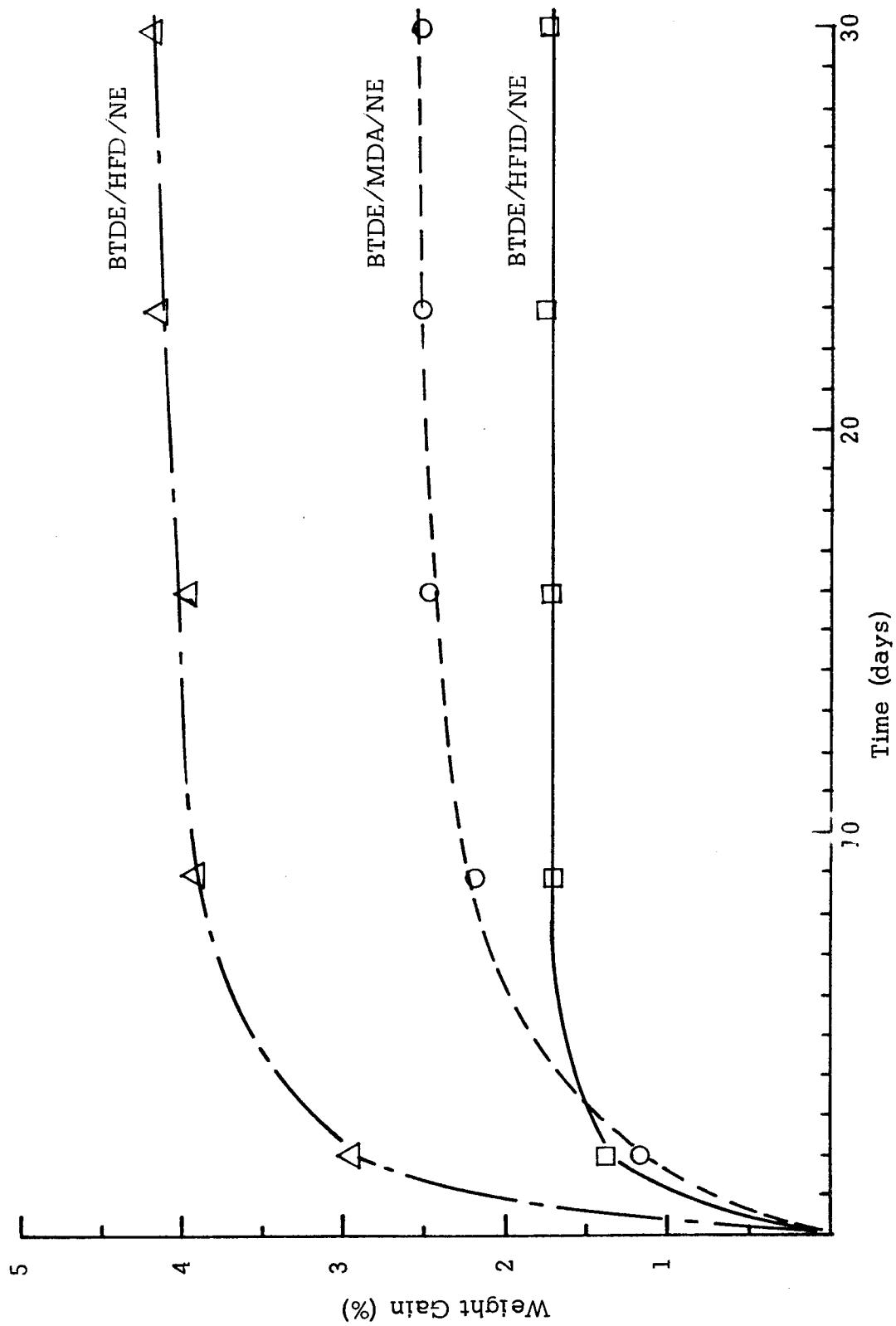
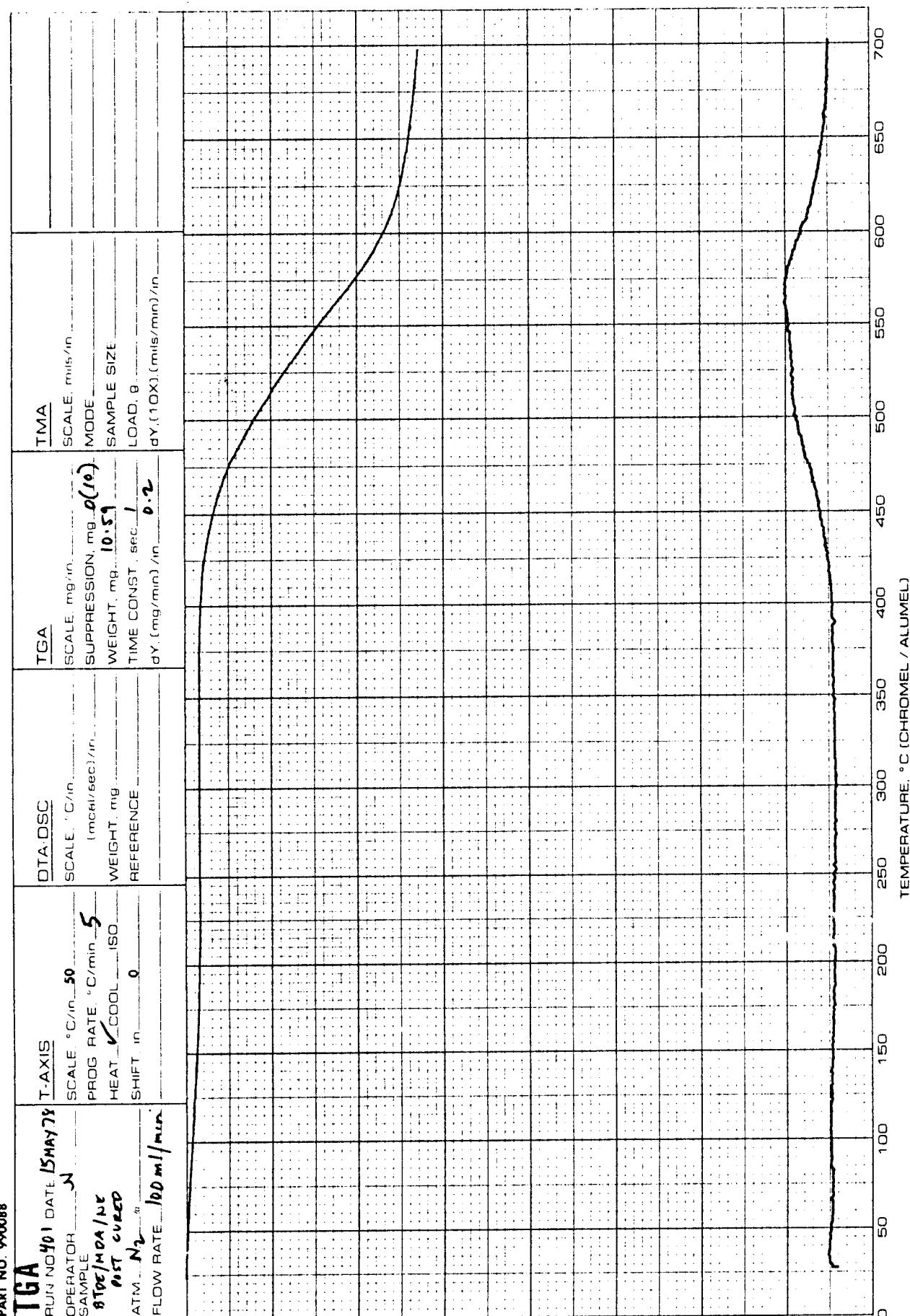


Figure 3: Weight Gain as a Function of Time of Fully Cured Resins on Exposure to 95% Humidity.

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MEASURED VARIABLE

Figure 4: TGA Scan of Post Cured BTDE/MDA/NE Resin (in Nitrogen)

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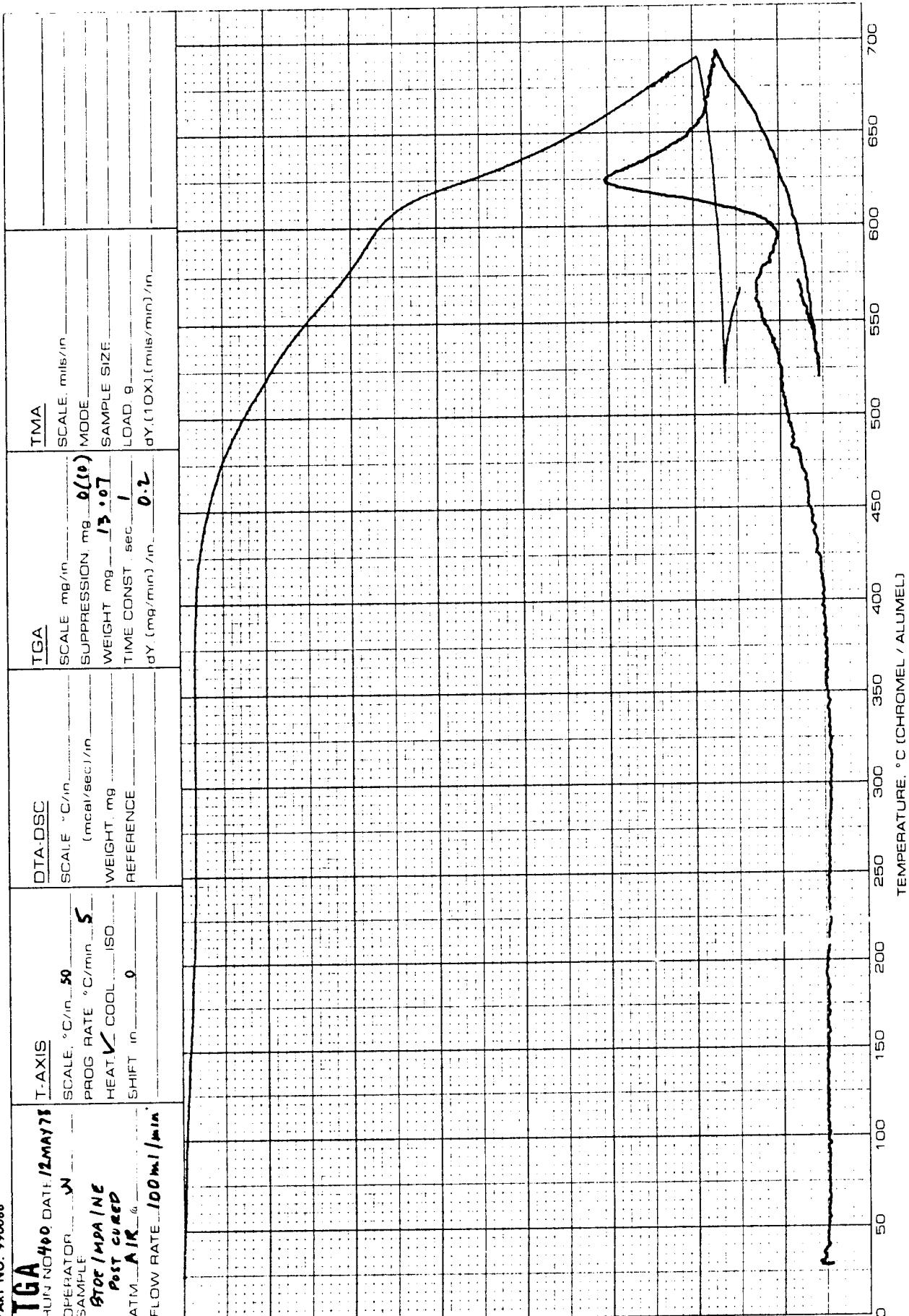
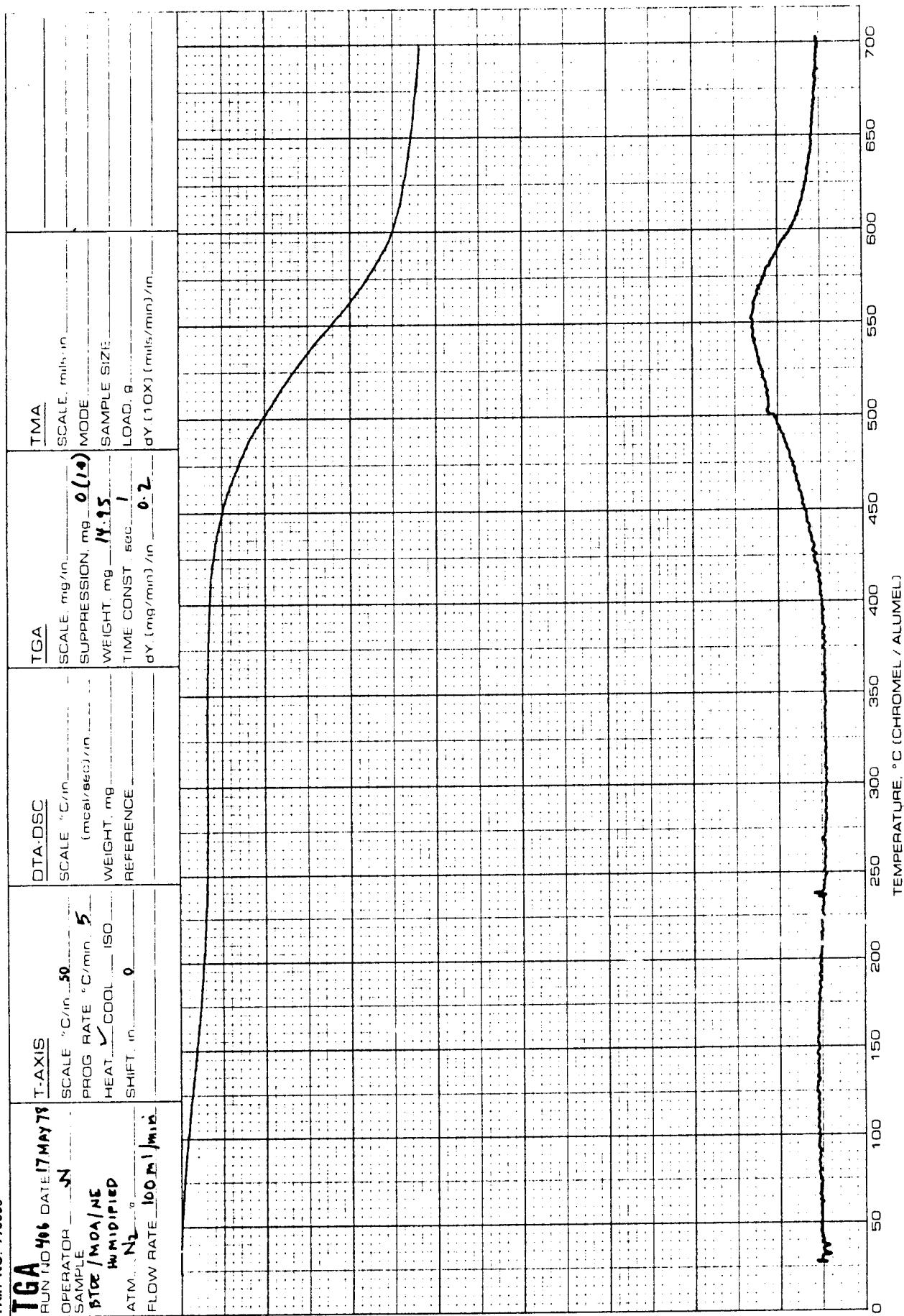


Figure 5: TGA Scan of Post Cured BTDE/MDA/NE Resin (in Air)

PART NO. 990088



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Figure 6: TGA Scan of Post Cured-Humidity Exposed BTDE/MDA/NE Resin (in Nitrogen)

PART NO. 990088

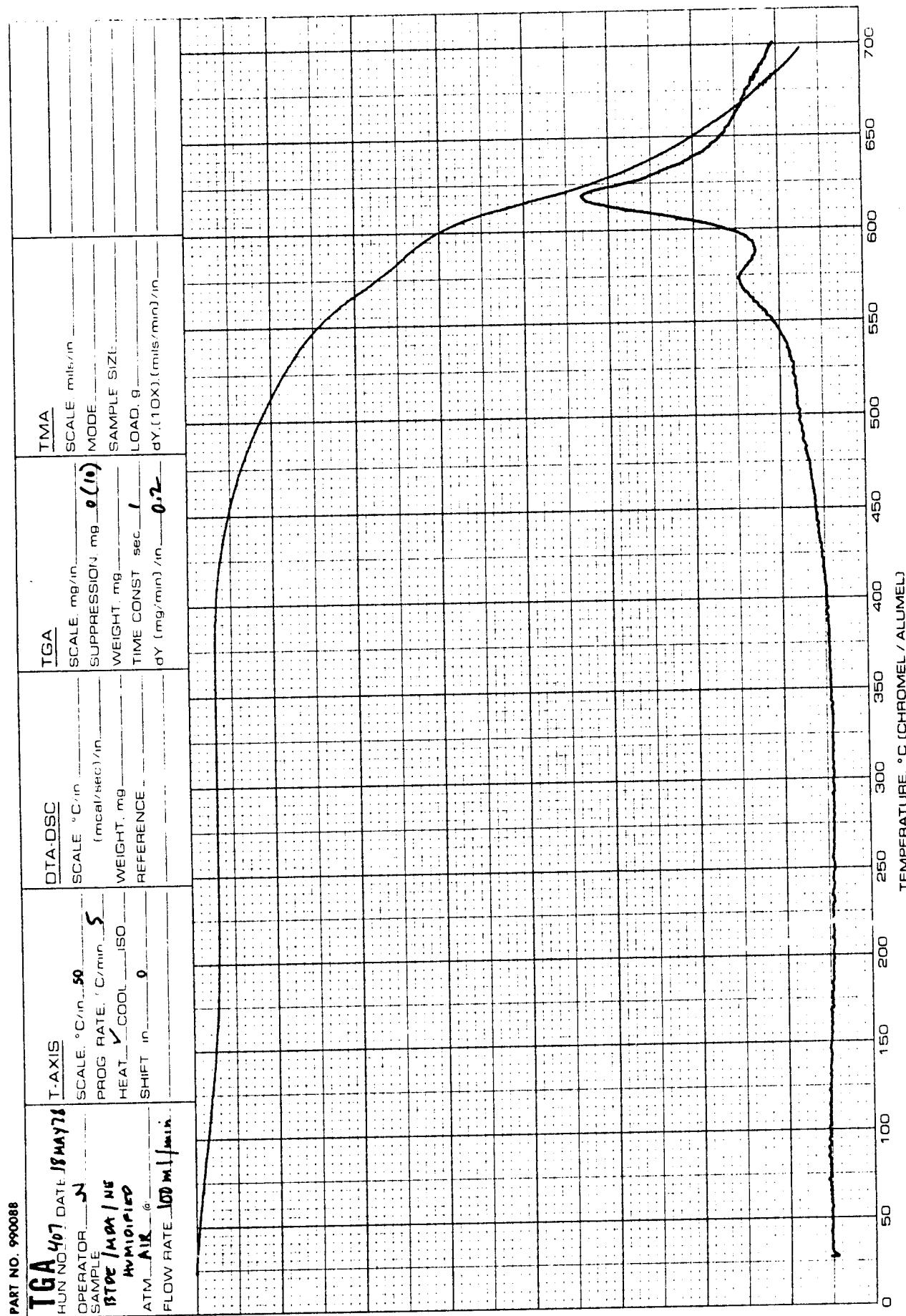


Figure 7: TGA Scan of Post Cured-Humidity Exposed BTDE/MDA/NE Resin (in Air)

PART NO 900088

**TGA** RUN NO. 402 DATE 15 MAY 78

T-AXIS		TGA		TMA	
DEHEATOR	SCALE "C/in" 50	SCALE "C/in" 10	SCALE "mg/in"	SCALE "mils/in"	
SAMPLE	PROG. RATE. °C/min 5	(mcal/sec)/in	SUPPRESSION mg 0(10)	MODE	
STOVE / F2 O2 / HE	HEAT. ✓ COOL ISO	WEIGHT. mg 8.15	SAMPLE SIZE		
POOT Cured	SHIFT in 0	TIME CONST. SEC. 1	LOAD. g 9		
ATM N2	FLOW RATE 100 ml/min	dY (10X) (mils/min) /in 0.2	dY (mg/min) /in		

TEMPERATURE, °C (CHROMEL / ALUMEL)

0 50 100 150 200 250 300 350 400 450 500 550 600 650 700

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### MEASURED VARIABLE

Figure 8: TGA Scan of Post Cured BTDE/HFD/NE Resin (in Nitrogen)

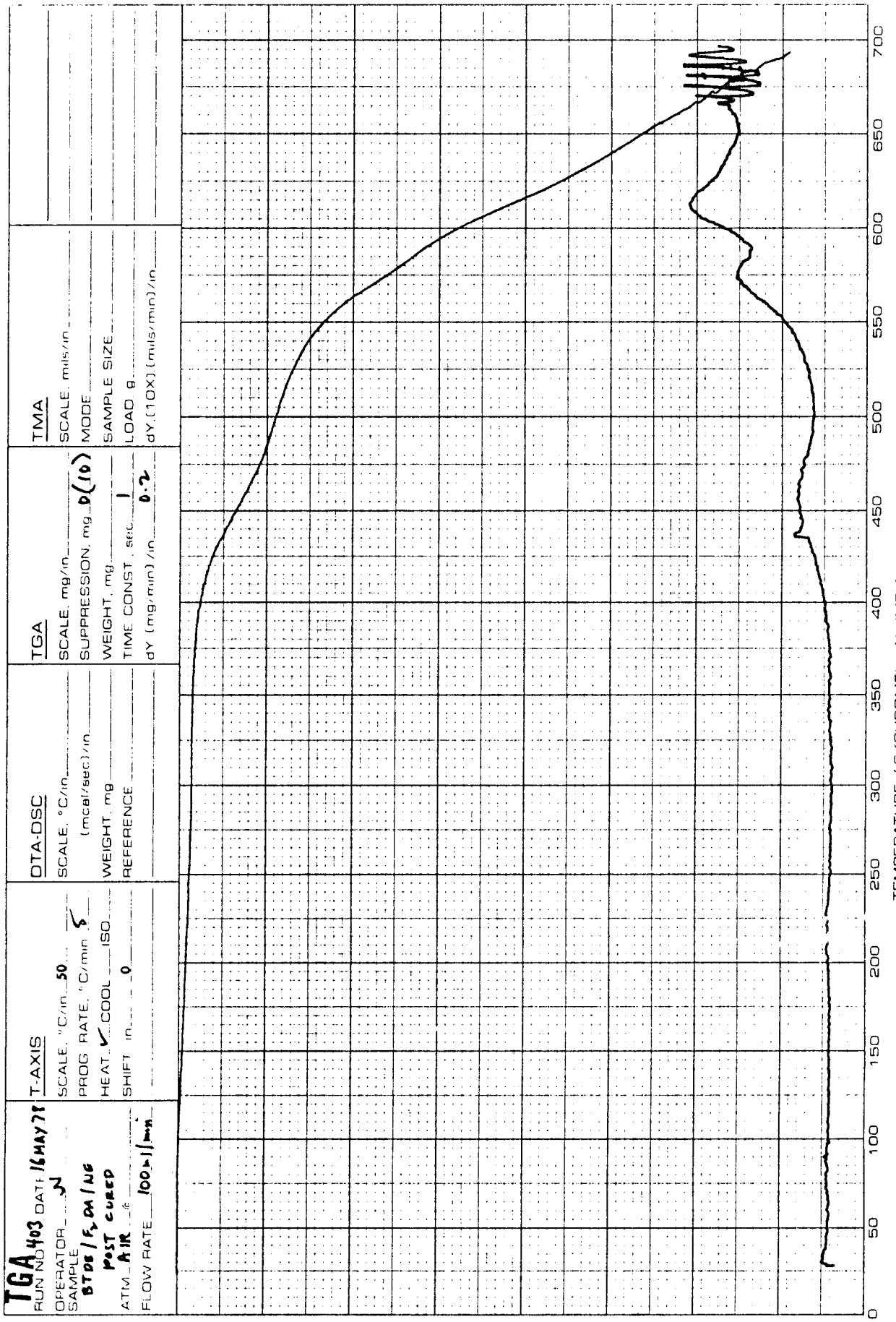
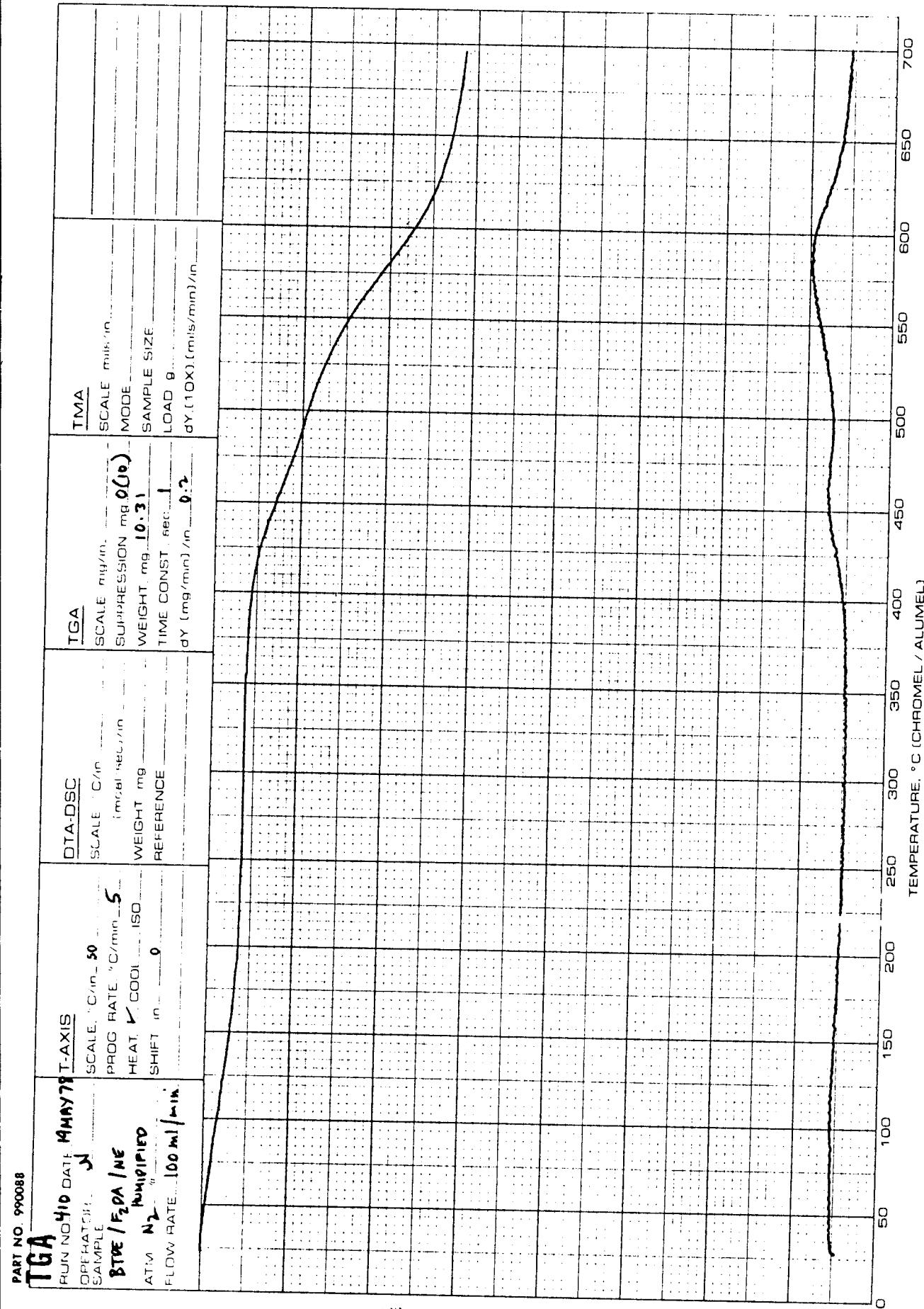


Figure 9: TGA Scan of Post Cured BTDE/HFD/NE Resin (in Air)



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Figure 10: TGA Scan of Post Cured-Humidity Exposed BTDE/HFD/NE Resin (in Nitrogen)

**TGA** BUN NO 411 DATE 22 MAY 74 T-AXIS  
 OPERATOR **JN** SCALE **1** PROG R  
 SAMPLE **1** HEAT **✓**  
 SHIFT **1**  
**BOTT/FDA IN E** **100** **100**  
 ATM. **AIR** **100** **100**  
 FLOW RATE **100** **100**

<b>TGA</b>		<b>DATE 22 MAY 78</b>	<b>T-AXIS</b>
<b>Run No</b>	<b>411</b>	<b>OPERATOR</b>	<b>S</b>
<b>SAMPLE</b>	<b>BTOT / F201/N6</b>	<b>SCALE, "C/in</b>	<b>50</b>
<b>ATM.</b>	<b>Air</b>	<b>PROG RATE, °C/min</b>	<b>5</b>
		<b>HEAT</b>	<input checked="" type="checkbox"/> <b>COOL</b>
		<b>SHIFT, in</b>	<b>0</b>
		<b>FLOW RATE, 100 ml/min</b>	
		<b>REFERENCE</b>	

TMA	SCAL	MODI
TGA	SCALE mg/in sec/in	SUPPRESSION mg <u>0.10</u>
		WEIGHT. mg <u>9.41</u>
		TIME CONST sec <u>1</u>
		dy (mg/min) /in <u>6.2</u>

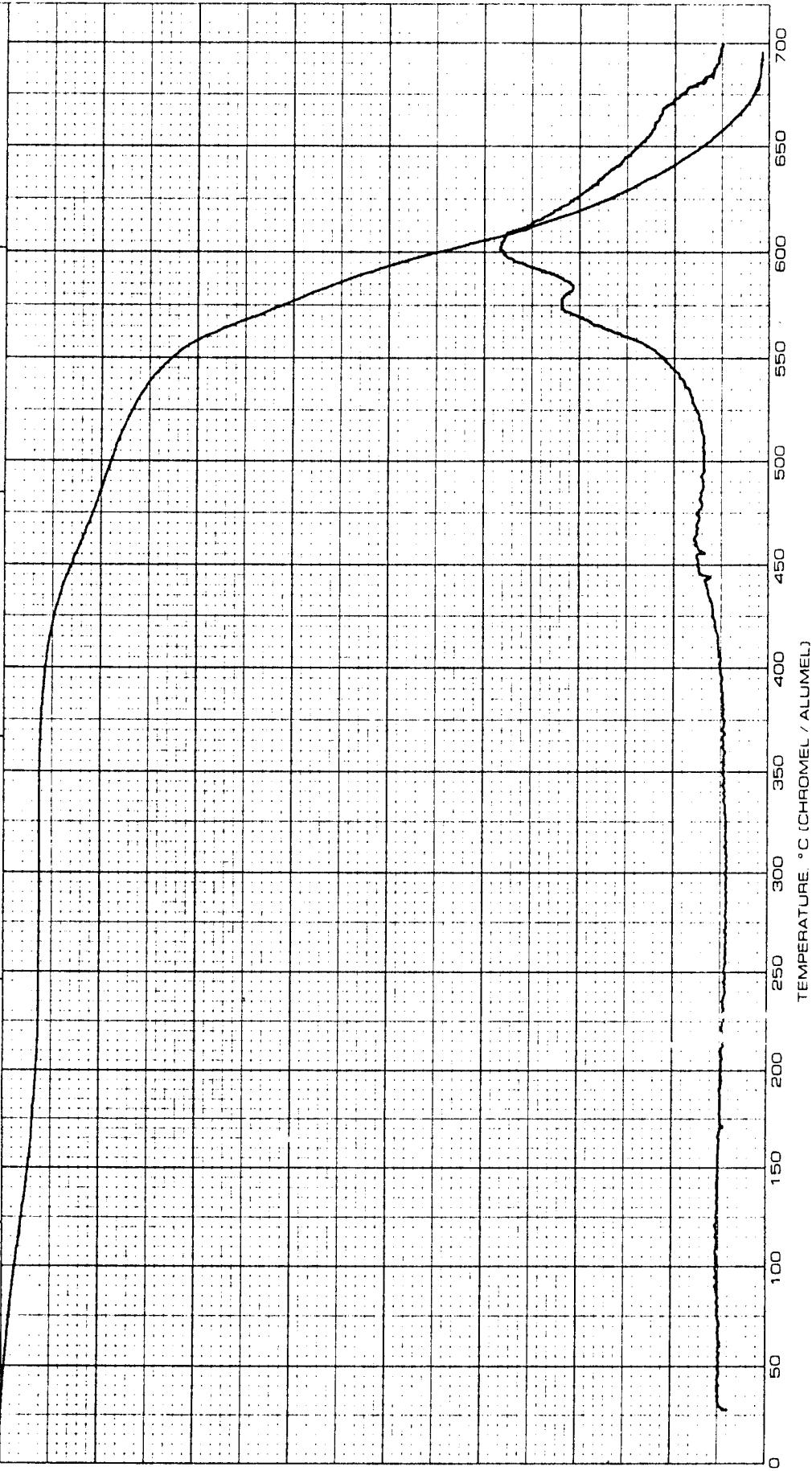
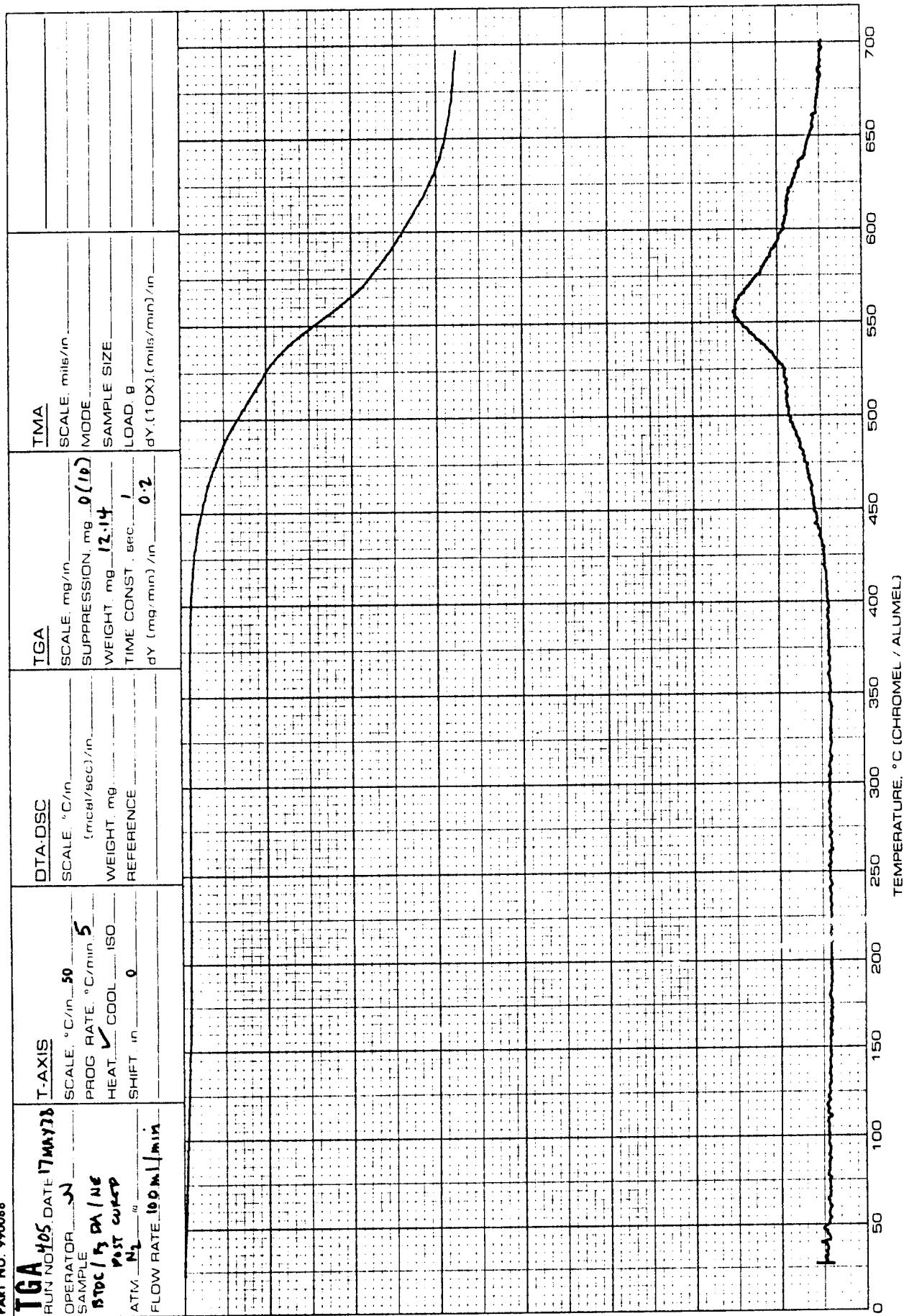


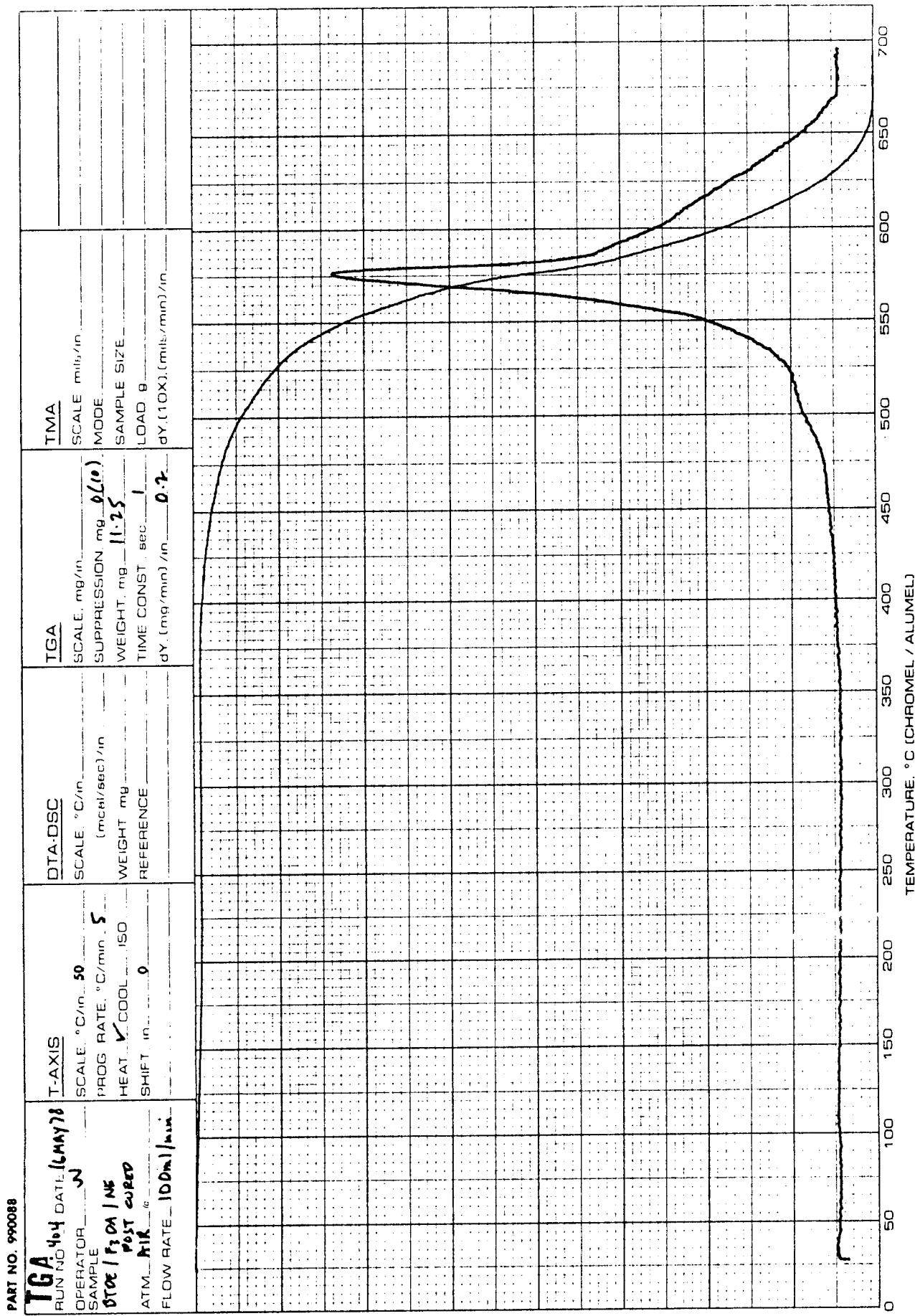
Figure 11: TGA Scan of Post Cured-Humidity Exposed BTDE/HFD/NE Resin (in Air)



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Figure 12: TGA Scan of Post Cured BTDE/NE Resin (in Nitrogen)

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Figure 13: TGA Scan of Post Cured BTDE/HFID/NE Resin (in Air)

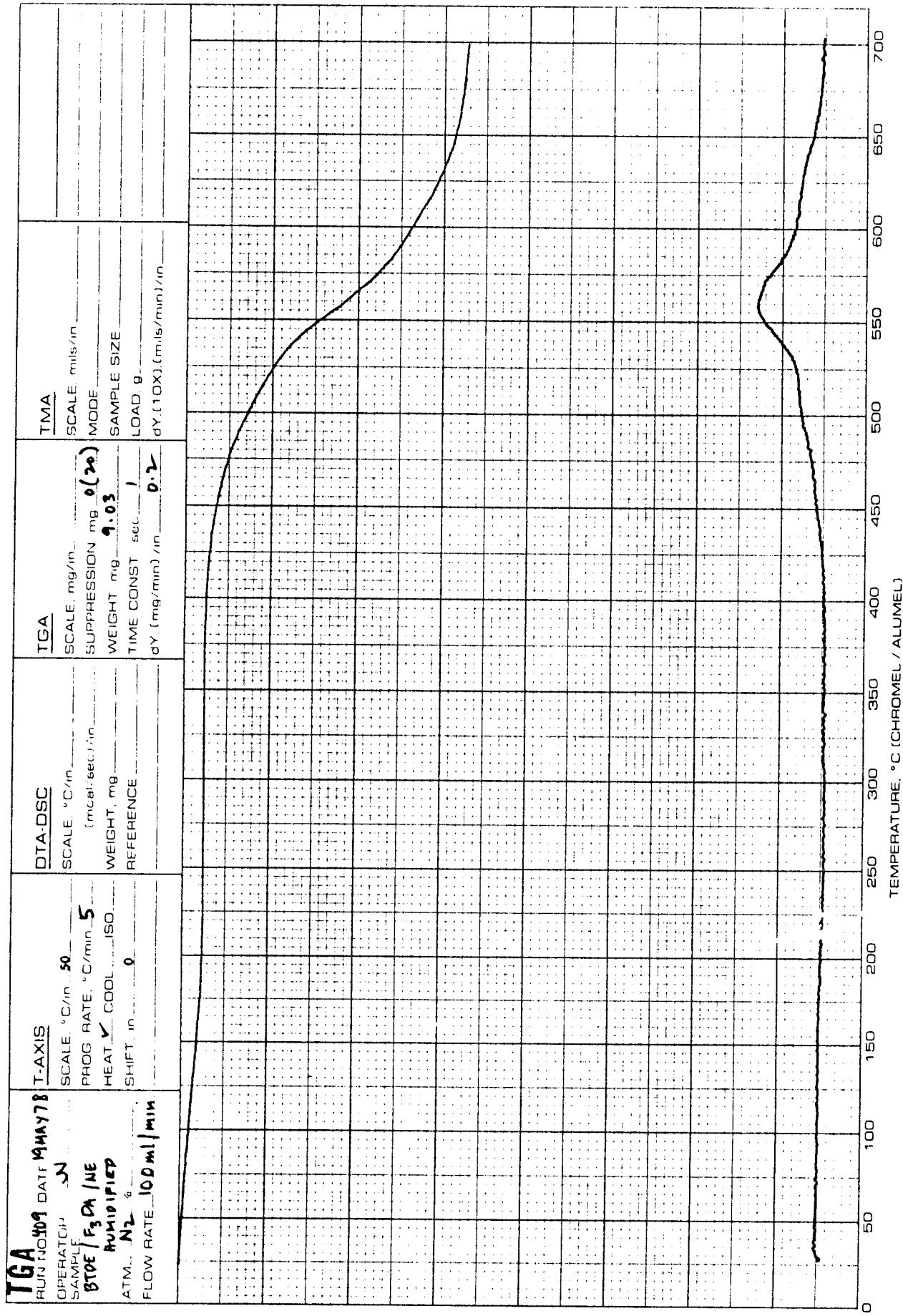


Figure 14: TGA Scan of Post Cured-Humidified BTDE/NE Resin (in Nitrogen)

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**TGA** RUN NO 463 DATE 18 MAY 78 T-AXIS

OPERATOR <b>JN</b>	SCALE °C, in. 50	DTA-DSC	TGA
SAMPLE <b>BTDC / F3 PA / NE HUMIDIFIED</b>	PROG RATE °C/min 5	SCALE °C/in. (ml/ats/sec)/in. 1	SCALE mg/in. (10)
ATM <b>AIR</b>	HEAT ✓ COOL ISO	WEIGHT mg 13.45	SUPPRESSION mg 0 (10)
FLOW RATE 100 ml/min	SHIFT in. 0	TIME CONST SEC 1	WEIGHT mg 13.45
	REFERENCE	dy (mg/min) / in 0.2	TIME CONST SEC 1

**TMA**

SCALE mils/in. (10)	MODE
SAMPLE SIZE	LOAD 9
dy (100X). (mils/min)	dy (100X). (mils/min)

TEMPERATURE °C (CHROMEL / ALUMEL)

### MEASURED VARIABLE

45

Figure 15: TGA Scan of Post Cured-Humid Exposed BTDE/HFID/NE Resin (in Air)

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